F. B. Hobart

A Colorimetric Method for the Estimation of Cobalt

A COLORIMETRIC METHOD FOR THE ESTIMATION OF COBALT

BY

FLOYD BEATTY HOBART

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Floyd Beatty Hobart

ENTITLED A Colorimetric Method for the Estimation of Cobalt.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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S. A. Braley
Instructor in Charge

APPROVED : W. A. Noyes

HEAD OF DEPARTMENT OF Chemistry

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I. INTRODUCTION.

PURPOSE OF THE INVESTIGATION. It was observed by Dr. S. A. Braley a few years ago that in testing qualitatively for nickel with dimethyl glyoxime in a solution which he found did not contain nickel, but which did contain cobalt, that the solution became brown. He decided that this must be due to the formation of a salt of cobalt dimethyl glyoxime which was soluble. He verified this and found further that if both nickel and cobalt were present, it was possible to filter off the nickle precipitate and still have the brown cobalt color left in the filtrate and that apparently there was no diminishing of the cobalt color in the presence of the nickel.

Therefore, at the suggestion of Dr. Braley, this investigation was carried out to determine if the brown color of the solution, obtained by the addition of dimethyl glyoxime to a cobalt salt solution, was directly proportional to the quantity of cobalt present or not, and if this was true, to work out a scheme whereby the amount of cobalt could be colorimeterically estimated.

HISTORICAL. There is no record of previous work on Cobalt dimethyl glyoxime salts or solutions and with the exception of the following statement of Böttger[1] that, "cobalt salts give with dimethyl glyoxime a brown colored compound", there is no mention in the literature of the reaction of cobalt with dimethyl glyoxime alone. Treadwell[2] and Mellor[3] in their texts on analytical chemistry both state that before determining nickel with dimethyl glyoxime, that the nickel solution must be diluted so that not more than .1 gram of cobalt is present in 100 cc. of solution, but both fail to explain why this should be done. They have no doubt noticed that cobalt in greater quantities than this will

give a precipitate with dimethyl glyoxime.

There has been some little work on the complex cobalt dimethyl glyoxime salts. Tschugaev[4] discusses several complex salts of cobalt dimethyl glyoxime having ammonia or pyridine attached to the molecule by auxiliary valences. In these salts, the cobalt has three valences and two auxiliary valences.

Matsui[5] explained how he has been able to get cobalt to react with dimethyl glyoxime in nickel and iron free solutions by adding $(NH_4)_2S_x$. He also obtained an orange-red double salt of cobalt-lead dimethyl glyoxime which he was able to isolate.
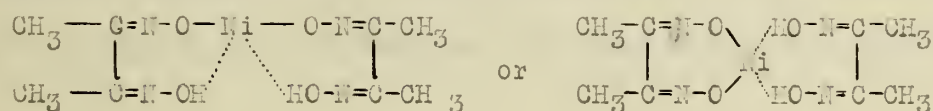
Tschugaev was the first to notice that nickel with dimethyl glyoxime gave a red precipitate. He made this known in 1905 and said that .1 gm. of nickel might be determined in the presence of 500 gms. of cobalt[6]. The structure of nickel dimethyl glyoxime was first worked on by F. W. Atack[7] and later by Tschugaev,[4] who also worked on the complex glyoxime salts of cobalt and proved their structure. This work is all of rather recent date.

In 1907 Brunck[8] published the present method for determining nickel with dimethyl glyoxime in ammoniacal solution and later in the same year a second article[9] giving the method for the determination in acetic acid solution using sodium acetate to neutralize the mineral acid present and thus form the acetic acid. In this paper he advocates that the ferric ion if present should be reduced to the ferrous state by the use of H_2SO_3 before adding the other reagents.

Other than this there has been no work done on the dimethyl glyoxime salts of cobalt or nickel.

II. THEORETICAL.

Theoretically there is nothing new in this procedure. Since cobalt and nickel are so closely related it is safe to assume that they will react in the same manner with dimethyl glyoxime, and that the structural formula of the two salts will be identically the same. Tschugaev has studied the reactions and the structure of the salts of the glyoximes and gives his theories and proofs in his paper on the "Chemical Constitution of the Dioximes"[4]. The majority of his work was on the nickel salts but he did enough work on the complex cobalt salts to show without doubt that they were capable of forming similar compounds. He explains that the reaction of nickel with two molecules of dimethyl glyoxime may give a salt of either of the two following structures:

$$
\begin{array}{c}
CH_3 - C = N - O - Ni - O - N = C - CH_3 \\
| \quad\quad\quad\quad\quad\quad\quad\quad | \\
CH_3 - C = N - OH \quad\quad HO - N = C - CH_3
\end{array}
\quad or \quad
\begin{array}{c}
CH_3 - C = N - O \quad\quad HO - N = C - CH_3 \\
| \quad\quad\quad\quad Ni \quad\quad\quad | \\
CH_3 - C = N - O \quad\quad HO - N = C - CH_3
\end{array}
$$

The dotted lines indicate auxiliary valances, for which the theory has been advanced by Werner.[10] Of these two structures Tschugaev explains that there is more in favor of the former than for the latter and expresses himself as supporting the former, although he says that there is a great deal to be said in favor of the latter. He assumes that dimethyl glyoxime ionizes into the $\left[\begin{array}{c} CH_3 - C = N - O \\ | \\ CH_3 - C = N - OH \end{array}\right]^{-}$ ion and the H^+ ion and that the nickel replaces the H in two molecules of the dimethyl glyoxime. The auxiliary valence unites the anion with the other hydroxyl group of each molecule and thus prevents it from ionizing to give a free H^+ ion. If this were not true the nickel would unite with only one molecule of dimethyl gloxime.

From the above it is seen that if dimethyl glyoxime were added

to any ordinary mineral acid salt of nickel or cobalt we would get this

equation: $2\left[(CH_3)_2C_2(NOH)_2\right] + NiCl_2 \rightleftharpoons 2\left[(CH_3)_2C_2(NO)_2H\right]Ni+$

2HCl and the free mineral acid being highly ionized would give an excess

of H^+ ions, and drive the reaction to the left. But if this solution

is made alkaline with NH_4OH we will have formed NH_4Cl and H_2O in place of

the HCl, and the presence of this NH_4Cl will drive out all of the H^+ ions

and cause the reaction to go to completion to the right, thus giving a pre-

cipitate of Nickel dimethyl glyoxime or in case a cobalt salt is used

instead of nickel we will get the cobalt dimethyl glyoxime salt. But since

this salt is very soluble, unless there is a large amount of cobalt pre-

sent, we will have no precipitate, but instead the clear brown solution

which is characteristic of cobalt dimethyl glyoxime.

Again if instead of using NH_4OH we use $Na C_2H_3O_2$ we will have

formed unionized acetic acid and NaCl and will again drive the reaction to

the right.

III.   EXPERIMENTAL.

Materials.   From pure Co CO_3 and $NiCO_3$ salts made by Kohlbaum, standard solutions of $CoSO_4$ and $NiSO_4$ were made containing about one gram of metal in one hundred cubic centimeters of solution. These solutions which were very slightly acid were standardized by electrolytic analysis.   During the process of the investigation portions of these standard solutions were diluted to obtain solutions desirable for carrying on the work.   Considerable quantities of ten per/sodium acetate in
cent
aqueous solution and of one per cent dimethyl glyoxime in alcoholic solution were used.

Apparatus.   A Duboscq dipping colorimeter of the ordinary type as found described in the various texts on analytical chemistry was used. This consists of two upright cylinders into which the solutions to be observed are poured, and through which rays of light are passed, by means of a mirror, and on into a telescope where they are reflected on to a pair of mirrors. By looking into the telescope these two mirrors may be seen and the colors reflected upon them compared. There are two more closed cylinders which extend down into the two already mentioned, and which may be removed up or down by means of a screw carrying a vernier scale. By turning this screw the thickness of the column of liquid may be varied until the colors reflected into the telescope are equal, and this thickness may then be read on the scale.   We will then find that W_1 is to W_2 as d_2 is to d_1 Where W 1 and 2 equals the quantity of salt in the respective solutions and d 1 and 2 represents the thickness of the respective solutions.   If W_2 is a known solution and W_1 an unknown, $W = \dfrac{W_2\ d_2}{d_1}$.   This is provided that the solutions are of equal volumn.   It will be found that the volumn of the unknown solution will us ally be greater than that of the

known solution and in this case the correction may be made by simply dividing d_1 by the quotient of d_2 into d_1. Then $W_1 = \dfrac{W_2 \; d_2}{\dfrac{d_1}{x}}$ where x equals the quotient of d_2 into d_1.

Method. The first procedure used was the one given in Treadwell Hall for the determination of nickel with dimethyl glyoxime in ammoniacal solution, with a few changes. The weakly acid solution of $CoSO_4$ was made slightly alkaline with NaOH and then acid with a few drops of acetic acid; it was then heated just to the boiling point and dimethyl glyoxime added in excess. As was expected a clear brown colored solution was obtained, since there was insufficient cobalt present to exceed the solubility of the cobalt dimethyl glyoxime salt. NH_4OH was next added drop by drop until the odor persisted. This caused the color to darken, showing that the reaction was driven to the right. At this point if nickel were present it would be filtered off, but since the solution contained cobalt alone it was only necessary to dilute it to a given volumn and transfer it to the colorimeter. Before doing this concentrated HCl was added, various amounts being used in different determinations. This was done because the color is not stable in ammoniacal solutions; they will darken for a few hours and then get lighter again, and it was thought that the addition of the acid would, by forming an excess of H^+ ions cause the solution to fade a certain amount and then remain constant. To determine if this was true or not a cobalt solution containing .00862 grams in 100 cc. was made as described above. Ten cubic centimeters of concentrated HCl were added to this and it was read again -st similar fresh solutions at intervals of one hour. The amount of fading is shown by the following data:

| | Known fresh sample | Readings of original sample at indicated intervals. | | | | | | |
		Zero	1 hr.	2 hrs.	3 hrs.	4 hrs.	5hrs.	7hrs.	27 hrs.
Reading	20	20	23	22	21.6	21.4	21.0	21.0	19.0

This proved that consistent results are impossible in HCl solutions and acetic acid was substituted in its place on account of its slight ionization. A few of the results are shown in the following table:

Sample X	Known	NaOH	$HC_2H_3O_2$	Di.Me.	NH_4OH	$HC_2H_3O_2$	Readings X	K
.00862 gms.		Alk.	acid	5 cc.	alk.	10 cc.	30.0 mm.	
	.00862 gms.	"	"	"	"	"		50.0 mm.
.01724 gms.		"	"	"	"	"	9.0 mm.	
	.00862 gms.	"	"	"	"	"		30.0 mm.
.00862 gms.		"	"	"	"	Faintly	23.5 mm.	
	.00862 gms.	"	"	"	"	acid		30.0 mm.
.00862 gms.		"	"	"	"	"	15.0 mm.	
	.00431 gms.	"	"	"	"	"		30.0 mm.
.01724 gms.		"	"	"	"	"	10.0 mm.	
	.00431 gms.	"	"	"	"	"		40.0 mm.

This shows that the addition of $HC_2H_3O_2$ will give better results than that of HCl, but there are occasional inaccuracies which are not explainable.

The sodium acetate method was next tried. The method is as follows: To a slightly mineral acid solution of a cobalt salt sodium acetate is added in sufficient quantities to drive out all of the H⁺ ions and give a neutral solution. This solution is heated just to the boiling point and dimethyl glyoxime added in excess, it is allowed to cool slowly, diluted to a given volumn and poured into the colorimeter without adding other reagents. The following data will explain the results:

(See next page)

Sample X	Known	$NaC_2H_3O_2$	Di. Me. Glyoxime	Vernier X	Readings K
.00862 gms.	.00862 gms.	10.0 cc.	5 cc.	20.0 mm.	
		10. cc.	5 cc.		20.0 mm.
.00862 gms.		40. cc.	10 cc.	20.0 mm.	
	.00862 gms.	15. cc.	10 cc.		20.0 mm.
.00862 gms.		20. cc.	5 cc.	20.0 mm.	
	.00862 gms.	5. cc.	5 cc.		20.0 mm.
.00862 gms.		20. cc.	30 cc.	27.5 mm.	
	.00862 gms.	20. cc.	10 cc.		20.0 mm.
.00862 gms.		20. cc.	25 cc.	26.4 mm.	
	.00862 gms.	20. cc.	10 cc.		20.0 mm.

Data obtained by applying the above two methods to solutions containing both nickel and cobalt salts is given in the following tables.

Ammoniacal solutions acidulated with acetic acid.

Ni. Pres.	Ni. Found.	Co. Pres.	Di.Me. Gl. added	Readings K	X	Co. Found
.0468 gms.	.0462 gms.	.00862 gms.	40 cc.	30.0	13.0	.00958
.0468 gms.	.04659 gms.	.00862 gms.	40 cc.	6.0	28.5	.00093
.0468 gms.	.04663 gms.	.00431 gms.	40 cc.	28.0	30.0	.00403
.0468 gms.	.04638 gms.	.001724 gms.	40 cc.	15.0	40.0	. 00162

K equals .00431 gms. Co. 5cc. DiMe. Gl.   All vols. 100 cc.

The Sodium Acetate method.

.0468 gms.	.04664 gms.	.00862 gms.	30 cc.	20.0	22.0	.00822
.0468 gms.	.04657 gms.	.00862 gms.	30 cc.	20.0	22.0	.00822
.0468 gms.	.04662 gms.	.00431 gms.	30 cc.	20.0	45.0	.00383

IV.   DISCUSSION OF RESULTS.

Several points were noticed while obtaining the data, which are not shown in the tables given.   In the first method it was found that the addition of acetic acid to fresh ammoniacal solutions would cause them to darken slightly and that these solutions would not fade to any appreciable amount for a few hours, although they would fade a great deal on long standing.   It was also found that if the ammoniacal solutions were allowed to stand for some time before adding the acid that they would darken somewhat and that then they would not change on the addition of acetic acid.   A large number of determinations were made with acetic acid solutions to learn the effect of different concentrations of acid and to confirm the darkening and fading of the solutions.   The results show that the quantity of acid does not matter provided that it is sufficient to acidulate the solution and that very good checks are usually obtained by this method although as is shown in the tables an occasional run will be far from correct.   This cannot be accounted for unless it is due to the rate of cooling the solutions.

The second or sodium acetate method brought out rather surprising results.   First, it was found that the brown cobalt color is more intense in sodium acetate solution than in acetic acid solution, and it would seem from this that the reaction is more nearly quantitative in this solution.   Second, it was found that if after adding the dimethyl glyoxime the solution is cooled quickly as by whirling it in a flask under running water it will be only about half as intense in color as if it is allowed to cool slowly.   It was also found that the solutions which cooled slowly were very stable and did not change color even on long standing

while those which were cooled quickly would continue to darken until they had reached the same intensity as the other solutions. This required from 75 to 100 hours. The addition of strong mineral acids causes no change in color other than from the effect of dilution, unless the solutions are boiled, in which case they will fade very rapidly. There is therefore no reason for adding acid to the solutions and the only reagents necessary are sodium acetate and dimethyl glyoxime. From the experimentation it seems that too great an excess of $NaC_2H_3O_2$ is impossible and since an excess is absolutely necessary it is advisable to make this excess rather large. Varying quantities of dimethyl glyoxime will give varying results. A large excess will make the color lighter than it should be and if cobalt is present in rather large amounts an excess of dimethyl glyoxime solution will cause it to precipitate out in a very fine almost collodial brown precipitate. A large excess of dimethyl glyoxime should therefore be avoided.

From the investigation of pure cobalt solutions it would seem that the sodium acetate method ought to give better results with solutions containing both cobalt and nickel salts. This was confirmed by determining both metals from the same solutions using each method. The results as given in the last set of tables show the latter method to be the most consistent. Not only are the cobalt determinations better by this method but the nickel salt is much easier to filter from the acetate solution. The largest source of error seems to lie in the cooling of the filtrate and it is advisable to warm the suction flask and the Gooch crucible before filtering off the nickel salt.

V. CONCLUSION.

The result of this investigation proves that the color caused
by the addition of dimethyl glyoxime to a cobalt salt is directly propor-
tional to the quantity of cobalt present as long as this quantity is in-
sufficient to give a precipitate. The methods employed in this investi-
gation may be used to determine cobalt if it is present between the limits
of .0005 grams to .01 grams in one hundred cubic centimeters. With prac-
tice and care the error should not exceed .0002 to .0003 grams in the more
concentrated solutions. As the solutions become more dilute the per cent
of error will necessarily increase but since the results by the sodium
acetate method are always low a corrective factor may be applied if de-
sired and thus a greater degree of accuracy obtained than was thought
possible at the beginning of the investigation.

Copper and iron form colored salts with dimethyl glyoxime
in sodium acetate solutions and on this account it is impossible to
determine cobalt colorimetrically in the presence of these metals. How-
ever some indication may be obtained as to the qualitative estimation
of cobalt even in the presence of these metals although the results can-
not be taken as conclusive.

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